

1922

N 63



AN INVESTIGATION ON THE PRODUCTION OF LEAD  
ARSENATE BY ELECTROLYTIC METHOD

BY

ARATA LEO NITTA

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN CHEMISTRY

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COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1922



1922  
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*W. S. Putnam*

**Instructor in Charge**

APPROVED: *W. A. Noyes*

HEAD OF DEPARTMENT OF ..... *Chemistry* .....

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ACKNOWLEDGMENT

To Professor Nutnum, under whose direction this investigation was carried out, the writer wishes to express his gratitude for many valuable suggestions and kind guidance. Thanks are also due Dr. Dietricson, who by furnishing necessary apparatus, has made the laboratory work possible.

A very faint, large watermark-like image of a classical building with four prominent columns is visible in the background.

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## INSECTICIDES.

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### INTRODUCTION TO INSECTICIDES.

- a. Importance of Insecticides in industry--3.
- b. Classes of Insects and Insecticides--4.

### Historical.

- a. Origin of first insecticide in U.S.--5.
- b. Development of antiseptics and disinfectants--6.
- c. Initial insecticide industry--6.

### Chemical composition of commercial insecticides--6.

- a. Government classification--6.

### Industrial use of insecticides on man and animals and its raw materials--6.

### Experimental--7.

- a. Application of insecticides--7.

### Conclusion--8.



## IN INDIA.

The electrolytic process is a recent advancement in the manufacture of various pigments and some chemicals.

### References:-

"The Manufacture of Chemicals by Electrolysis" by A. J. He.

"Electrolytic production of white lead, cadmium yellow, of mercury vermillion, of Schiele's green, and of Berlin blue," in "Experimental Electrochemistry" by Hopkins, pp. 122-152.

Several patents have been granted on the manufacture of white lead by electrolysis.

U. S. 644,776 (1900) by Luckow.

"An Electrolytic Process for Manufacture of White Lead", by A. E. Williams, J. Am. Chem. Soc. (1905) p. 135.

"A Process of Manuf. Lead Salts b. Electrolysis" U.S. 678,438 (1901) by J. B. Libbitts.

"Method of Manuf. of Lead Salts b. Electrolysis" U. S. 17,508,948 b. W. M. Harrington (1919).

"White Lead by Electrolysis" b. A. H. Brown.  
U. S. 480,103 and 503,555.

and several others.



It is claimed that the electrolytic production of white lead has great advantages over the old processes of Dutch, French, or the Germans.

Why then the similar process can not be applied on the production of lead arsenate?

The investigation involves technical process based upon the chemical theories and the whole success moreover depends upon the economical standpoint of the manufacturing. In attacking the problem it is well, however, at the first hand to consider the successful production of lead arsenate without considering all the economical factors involved. After finding the favorable conditions of its manufacture the economical features, such as the cost of raw materials, amount of energy to be consumed, the cost of labor for the production, and the conditions should be considered.

The sphere of the work is wide and it requires a good knowledge of electrochemistry coupled with an ability in some researches.

A very simple preliminary survey on the subject and a little oil unrefined gasoline, test-oil, clear oil, the may happen to bump on the stumbling block in your future experiments.

Now in influencing conditions on the process to be investigated much foliage, etc.

I. Nature of the Electrolyte.

2. Concentration of Electrolyte.

3. Temperature influences considerably the process.



1. ~~Objectives~~.

1. Substitutionalities in the first job.
2. Write an incentive based remuneration.
3. Introduce a lateral placement.
4. Stability of employees based on better incentives.

2. ~~Objectives~~.

1. Restoring the facilities obtained.
2. Economic development of the economy, etc.



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### INFLUENCE OF INSECTS ON PLANTS.

Cultivation of lands or large-scale growing of plants is often attended by insects that injure the plants. The more highly developed become our agricultural arts, the more care is necessary to protect them from agencies which will hinder their growth. This is the reason that the most effective agricultural insecticides and fungicides have been of the highest importance lately.

### CLASSES OF INSECTS AND THEIR HABITS.—C. D.

There are two classes of insects; one that directly injures the plant it is eating in body. Some insects bite or chew the foliage or fruit of the plant to injure the plants. Another class of all kinds, however, eat out the plant tissue. These insects bore holes in the plant body, or eat out the seeds, roots, leaves, stems, flowers, etc. Insects are very small, and are usually winged, though some are wingless. They are also very numerous, and are found in almost every part of the world.

In the earlier stages of plants when there are no seedlings or young plants, the insects attack the leaves, stems, etc., and sometimes by one insect attacking a plant, the plant may die. Insects attacking the young seedlings of the plant, however, do not always kill the plant, but they do retard its growth, and make it smaller than it would have been if the insects had not attacked it.



The following is the result of the experiments made

The following is the result of the experiments made  
on the potato root. Take of the young sprouts  
and roots, including the potato similar to water, just  
as the country. It is found that when at first it  
appears to be green, which I would suppose is plant,  
should be used on the potato plants with good effect.  
Considerable attention was given to the roots of the  
potato, because it is said that in the potato there  
are many poisons in particular, which are injurious  
when exposed to the air. This will be evident that the  
water which the solution contains must have been assimilated  
by the potato itself. It is also observed that  
water, or another plants, that are planted near  
the potato are affected by the plants and become weak  
or plants are ruined.

After this on the potato plants, in  
the atmosphere, it was supposed that water by the  
plant had very little water soluble, water, slight  
and the water. It was originally found  
soluble in water and the water. It has  
been insoluble and this practically remains so v  
ery or soluble, it also has another point, that  
this point is that, if the water is added to the  
water from the water, solution, it adheres to the leaves  
and no water is added to the water. It is due to  
the roots, and its peculiarities. It could be used



of the salt solution, and on heating was soluble  
either in the water or by the addition of a few drops of  
water, and was a light yellow powder.

#### LEAD CHROMATE SPRAY ON THE SPARK PLATE.

This is bright, shiny, & dry, and is made at  
least by such acids without much or any hydrochloric acid; -  
mostly by mixing the solutions of sodium chromate and lead  
acetate. The precipitate is dried and screened if the whole  
mixture is then poured into the spray tank for the use.

#### LEAD CHROMATE MIST.

The first successful commercial manufacture was  
carried out by Cornelius D. Vreeland of Montclair, N. J.  
In September, 1906, he had application for a patent covering  
an electrolytic method of preparing chrome compound of lead.

#### LEAD CHROMATE (L.C.)

One well known "Electro" brand manufactured in a  
little plant in Pottersville outside of Lehighton, Pa., is one  
of the best known in the market. The process is, how-  
ever, also one of the best.

The method of precipitation of lead chromate  
is as follows: the lead acetate, which has been made  
at several small plants, is suspended. Hydrochloric  
acid and lime are the fairly cheap raw materials.  
Intensive experiment on the use of the solid compounds stim-



lead arsenite came out as a commercial product.

Chem. Eng. 26, (1901) p. 331.

In 1905, the author and W. A. Volck, of San Onofre, California, got in a patent on the manufacture of lead arsenate by mixing arsenic acid and litharge.

U. S. 799,935, Aug. 3, 1909.

The mixture was roasted in presence of oxygen supplied by oxidizing agent. Lead arsenite, formed at the early stage, is oxidized into arsenate. Since that time more than a dozen patents are taken out on the subject.

Approximate chemical composition of commercial arsenate.

The raw material finds of lead arsenate possible. The original product was what is known as trilumbic arsenate of lead,  $\text{Pb}_3(\text{AsO}_4)_2$ .

Theoretically it contains

74.42 percent of Pb O.

15.58 " "  $\text{As}_2\text{O}_3$

in the other is ortholumbic arsenate, which contains theoretically

64.0 percent of Pb O

15.15 " "  $\text{As}_2\text{O}_3$

2.50 " "  $\text{L}_2\text{O}$



The commercial lead arsenate is a mixture of the above two oxides in different proportions, and this variation in the proportion due to the different methods of preparations. The value of the insecticide is determined by the amount of arsenic in the compound; and some of the best trade contain up to 50 per cent of arsenic oxide.

#### GOVERNMENT SPECIFICATION.

By the Insecticide and Fungicide Act of 1910, the powdery form of lead arsenate should not contain more than 50 percent of water. It should contain at least 12 1/2 percent of arsenic oxide, and less than 3/4 of one percent of arsenic oxide in water-soluble form.

Chem. Age, (1921) 23, no. 7, p. 557.

#### PATENT PROCESS OF MANUFACTURE OF ARSENATE LEAD AND ARSENATE.

The larger part, probably more than three-fourths of the arsenate of lead produced in this country, is made by the interaction of arsenic acid and litharge.

There are two distinct methods of manufacturing:- one being a wet process and the other, which is rather a recent invention, being dry method.

#### DRY METHOD:-

U. S. 1,344,035 (1920) by C. H. Nedenburg and D. W. Kratt.

U. S. 1,175,565 by L. Shepherd, (1916)



J. Ind. and Eng. Chem. 1, (1921) p. 551.

The raw materials commonly used, due to the cheapness are litharge and white arsenic. Some processes, however, claim certain advantages in using lead nitrate, white lead, lead peroxide, and lead acetate.

Current Quotations on Prices of Raw Materials Used.

	by carlot	1000 c. lot
Litharge per lb.	.07 1/2--.08	.061/2-.09
White arsenic "	.06- .061/4	.06 1/2--.07
Lead nitrate "	.----	.15---.20
Lead acetate "	-----	.10 5/8--.12 1/2

---

Lead Sr. chate (paste)"	.09--.09	1/2	.010--.011
Lead arsenate "	.06	1/2--.07	.07 1/2-.08
(in powder)			

Sodium nitrate .025 .026

Chem. Met. Eng. Sept. 1921.

Sodium arsenate per lb. 0.76

Quoted from price list of Mallinckrodt Chemical Works (1921)

Sodium arsenate C. + per lb. 40.50

J. B. Baker Chemical Company.



APPARATUS.

Apparatus used,-

Ammeter--weston direct reading ammeter, having  
reading of 55 amperes.

Rheostat--Carbon rheostat.

Voltmeter--weston direct current voltmeter having  
5 and 15 volts o. reading.

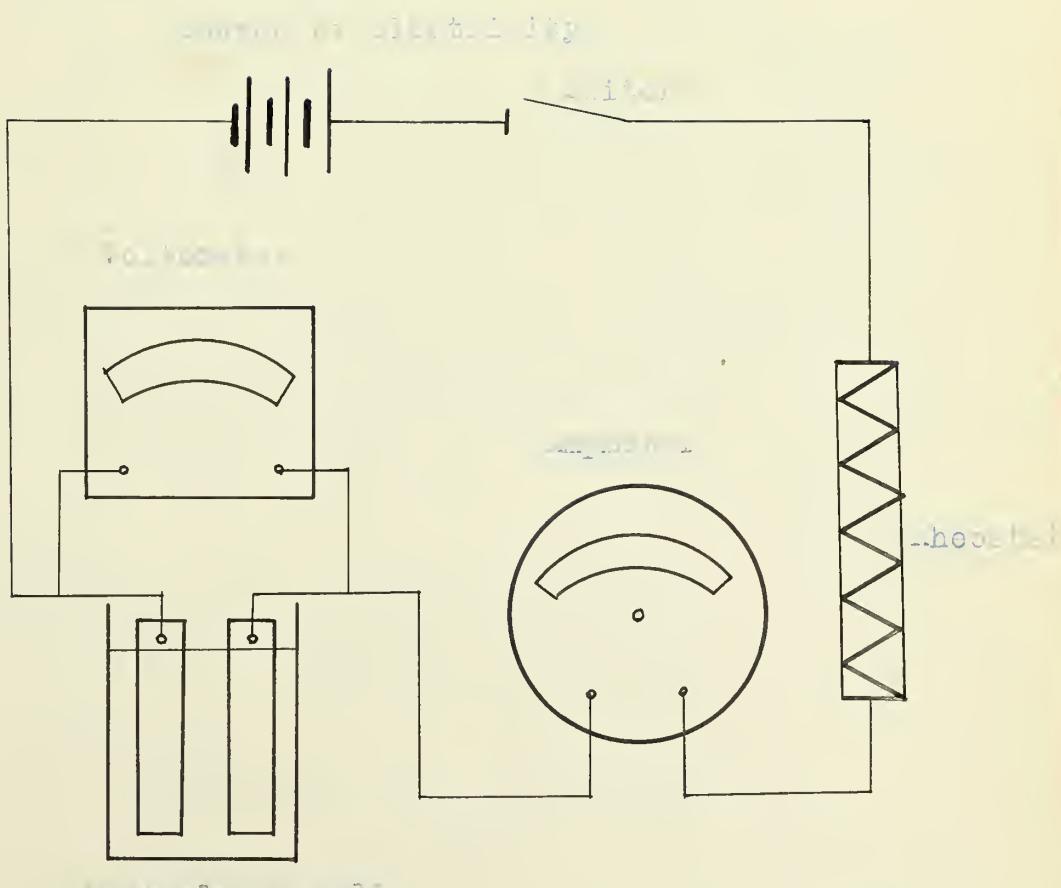
Electrodes used--carbon, iron, lead, and copper.

Cell jar-- One liter beaker is used.

Diaphragm-- A porous porcelain cup.

Source of electricity--from 110 volt direct current.

Diagram of apparatus.





EXPERIMENT ONE.

The first experiment based upon the theory of precipitation of insoluble lead arsenate in contact with arsenate ion from soluble arenate salts with lead ion electrolytically set free from the lead anode. The commonly known salts such as sodium arsenate and sodium biarsenate are tried.

The different kinds and different concentrations of electrolytes, various electrodes, and the effects upon the precipitation with various current densities were tested.

The following experiments were performed under fixed conditions only varying the electrolyte and its concentrations.

The fixed conditions are

Electrodes, - cathode, - Cu plate whose area  
being 1.7 dm. sq.

Anode, - - - b. plate whose area being  
2.6 cm. sq.

Current density, - 0.5 amp. per sq. dm.

Temperature, - at room temperature.

Duration of run, - 30 minutes,

Experiment 1.

Electrode used, - sodium biarsenate.

Concentration, - 5 per cent solution.

Observation, -

Hydrogen gas from the cathode.

Oxygen from the anode.



No precipitate was obtained.

#### Experiment 2.

Electrode used, - Sodium arsenite.

Concentration, - 5 per cent solution.

Observation, -

Evolution of the gases as in the preceding exp.

No precipitation was obtained.

#### Experiment 3.

Electrolyte used, - Sodium biarsenate.

Concentration, - 10 per cent solution.

Observation, -

Same as the proceedings.

#### Experiment 4.

Electrolyte used, - Sodium arsenite.

Concentration, - 10 per cent solution.

Observation, - Same as the proceedings.

#### The Effect of Secondary Salts.

The effect of the presence of secondary salt in the electrolyte was tested, as it was suggested by J. P. Carrier. He successfully used sodium chlorate or sodium acetate in the preparation of white lead from sodium carbonate solution with lead anode.



Trans. Am. Electro. Chem. Soc. (1904) p. 229.

C. S. 64, 779 by Richard and Koepfer.

Experiment 5.

Electrolyte used,-

50 parts of 5 per cent of sodium arsenate.

50 " " " " sodium chlorate.

Observation,-

Gases from the both electrodes.

No sign of precipitation.

Experiment 6.

Electrolyte used,-

50 parts of 5 per cent of sodium acetate.

50 " " " " sodium arsenate.

Observation,-

Same as the preceding.

Experiment 7,

Electrolyte used,-

50 parts of 5 per cent of sodium arsenate.

40 " " " " sodium acetate.

40 " " " " sodium chlorate.

Observation,-

Same as the preceding.



Summary of Experiment Series 1.

exp.	Electrolyte.	concent.	Observation.	Precipitation.
1.	Na <sub>2</sub> H As O <sub>4</sub>	5% sol.	Gases evolut. from electrodes.	no.
2.	Na <sub>3</sub> As O <sub>4</sub>	5 % sol.	"	"
3.	Na <sub>2</sub> H AsO <sub>4</sub>	10 % sol.	"	"
4.	Na <sub>3</sub> As O <sub>4</sub>	10 % sol.	"	"
5.	50 parts of Na <sub>3</sub> As O <sub>4</sub>	5 %	"	"
	50 " " Na <sub>2</sub> O <sub>3</sub> 5 %		"	"
6.	50 parts of Na <sub>3</sub> As O <sub>4</sub>	5 %	"	"
	50 " " Na COOCH 5 %		"	"
7.	20 pts. of Na <sub>3</sub> As O <sub>4</sub>	5 %	"	"
	40 " " Na COOCH	"	"	"
	40 " " Na ClO <sub>3</sub>	"	"	"



MARILLIUM 2.

The conditions being the same, the effect on various concentrations of electrolyte was tested.

Experiment 1.

Electrolyte, -500 CC. Of 1% of  $\text{Na}_3\text{AsO}_4$  sol.

Observation,-

The gases from the both electrodes.

No precipitation.

Experiment 2.

After 15 minutes of electrolysis of the experiment 1, 5 grams of sodium arsenate is added.

The observation and the results are the same.

Experiment 3.

After 15 minutes of electrolysis of experiment 2, 5 grams of sodium arsenate is added.

Observation,- No precipitation, but slightly cloudy.

Experiment 4.

The filtrate of the experiment of 3 is electrolyzed for 15 minutes after addition of 5 grams of sodium arsenate.

Observation,- Became very much cloudy.

Weight of the precipitate obtained 0.1042 gm.



Experiment 5.

After 15 minutes of electrolysis of experiment 4, filtered. To filtrate 5 grams of sodium arsenate is added, and electrolyzed.

Observation,- No precipitation.

Experiment 6.

After 15 minutes of electrolysis, 10 grams of sodium arsenate is added.

No precipitation.

Experiment 7.

After 15 minutes of electrolysis, 15 grams of sodium arsenate is added.

No changes from the preceding experiment was observed.

Summary for the experiment series 2.

The small amount of precipitation was obtained in experiment 5 and 4, whose concentrations are 3 and 4 respectively.



EXPERIMENT SERIES 3.

The effect of the varying proportion and the concentrations of the electrolyte and of the secondary salts is determined.

The fixed conditions are the same with series 1 experiment.

The quantity of electrolyte taken in each experiment is 500 cc.

The electrolyte was kept in acidic condition with nitric acid and indicator, in order to prevent the formation of basic lead salt.

Air is bubbled through the electrolyte in order to stir the precipitates formed.

Experiment 1.

Electrolyte,- 2 pts. of 5% of sodium arsenate.  
5 " " 5 " " potassium chlorate.

Observation,-

Voltage drop, -5.0 v. initial, 6.5 v. final.

Hydrogen gas from the cathode and precipitates clinging to the anode.

Weight of precipitate obtained after 50 minutes of run, 2.3850 gm.

Experiment 2.

Electrolyte,- 2 pts. of 6% of sodium arsenate.  
5 " " 5 " " potassium chlorate.



ste.

Voltage drop, - initial 3.8 v. final 5.2 v.

wt. of precipitation obtained, 2.7825 gm.

Experiment 5.

Electrolyte, - 2 pts. of 10% sol. of sodium arsenate.  
3 " " 5 " " K-chlorate.

Voltage drop, - initial 4.7 v. final 5.8 v.

weight of precipitation, 2.7572 gm.

Experiment 4. Changing the concentration of K-chlorate.

Electrolyte, - 2 pts. of 5% of K-chlorate.  
3 " " 5 " " sodium arsenate.

Voltage drop, - initial 7.0 v. final 7.9 v.

weight of precipitate obtained, 2.0876 gm.

Experiment 5.

Electrolyte, - 1 2 pts. of 6% of K-chlorate.  
15 " " 5 " " sodium arsenate.

Initial voltage drop, 4.9 v., final 5.5 v.

weight of precipitate obtained, 2.2564 gm.

Experiment 6.

Electrolyte, - 1 2 pts. of 10% of K-chlorate.  
15 " " 5 " " sodium arsenate.

Initial voltage drop 4.9 v., final 5.5 v.

weight of precipitate obtained 2.3605 gm.



Experiment 7. Increasing amount of K-chlorate.

Electrolyte, - (5 pts. of 10% of K-chlorate.  
(2 " " 5 " sodium arsenate.

Voltage drop, initial 8.2 v., final 8.6 v.

Weight of precipitation obtained 3.6342 gm.

Experiment 8.

Electrolyte (4 pts. of 10% of K-chlorate sol.  
(1 " " 5 " sodium arsenate.

Voltage drop, - initial 2.6 v., final 5.6 v.

Weight of precipitate 1.5582 gm.

SUMMARY FOR THE EXPERIMENT SERIES #3.

Exp.	Electro-	Conc.	Report.	Voltage drop.		Wt. of ppt.
				init.	final.	
1.	(Na <sub>3</sub> AsO <sub>4</sub> (K ClO <sub>3</sub>	5%	2 pts. 5 "	5.0	6.5	2.3820 gm.
2.	(Na <sub>3</sub> AsO <sub>4</sub> (K ClO <sub>3</sub>	6%	2 pts. 5 "	5.8	5.2	3.7825 "
3.	(Na <sub>3</sub> AsO <sub>4</sub> (K ClO <sub>3</sub>	10%	2 pts. 5 "	4.7	5.6	2.7572 "
4.	(KClO <sub>3</sub> (Na <sub>3</sub> AsO <sub>4</sub>	3%	2 " 5 "	7.0	7.9	2.0876 "
5.	(K ClO <sub>3</sub> (Na <sub>3</sub> AsO <sub>4</sub>	6%	2 pts. 5 "	4.7	5.9	2.2564 "
6.	(K ClO <sub>3</sub> (Na <sub>3</sub> AsO <sub>4</sub>	10%	2 pts. 5 "	4.9	5.5	2.3605 "
7.	(K ClO <sub>3</sub> (Na <sub>3</sub> AsO <sub>4</sub>	10%	3 pts. 5 "	8.2	8.6	3.6342 "
8.	(K ClO <sub>3</sub>	10%	4 pts.	2.6	3.6	1.5582 "



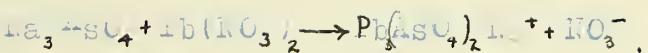
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C. S. 870,915 (1908)

The reactions involved in the reactions are



To the above solution sodium selenite is added.



Concentration, - 5 per cent solution of each.

-lectroac., -l. knowe, -l. loc. Ilite wioco area  
( S. J. sq. dm.



current density, - 0.5 amp. per 50 cm.

Duration of run, - 30 minutes.

After the run in each experiment, 10 percent solution of sodium arsenite is added until the solution is saturated and the solid ion is filtered, the precipitate then dried and weighed.

#### Experiment 1.

500 cc. of 5 percent sodium nitrate solution is taken.

Weight of precipitate obtained--7.3167 gm.

#### Experiment 2.

The filtrate from the experiment 1 is again electrolyzed for 30 minutes, and saturated with sodium arsenite, the precipitate was filtered and weighed.

Weight of ppt.--10.1765 gm.

#### Experiment 3.

The filtrate of experiment 2 is electrolyzed, and the precipitate is weighed.

Weight of precipitate--10.6362 gm.

#### Summary.

The process was initiated by addition of sodium arsenite, the weights of precipitate obtained are 7.3167 gm., 10.1765 gm., and 10.6362 gm. respectively.



### Experiment 5.

The solution contained the following:

The dried conditions were

Electrolyte, - 5 per cent of sodium arsenite.

Current density, - 0.3 amp. sq. cm.

Durration of run, - 30 minutes.

### Experiment 1.

Electrode used, - Lead cathode leaving area 0.166 sq. cm.

Voltage drop, - initial 6.0 v., final 5.6 v.

Weight of precipitate, - 1.526 gm.

### Experiment 2.

Electrode, - carbon block solution area 0.166 sq. cm.

Electrode potential, - initial 9.0, final 8.0 v.

Weight of precipitate, - 0.785 gm.

### Experiment 3.

Electrolyte, - copper sulfate solution area 1.7 sq. cm.

Electrode potential, - initial 9.0, final 8.0 v.

Weight of precipitate, - 1.048 gm.

### Experiment 4.

Electrode, - iron 100 mole chlorine area 0.166 sq. cm.

0.7 sq. cm.

Electrode potential, - initial 12.0 v. final 11.0 v.



Weight of precipitate obtained, - 1.6556 gm.

WELLING CL. AND S. G.

Carbon elect. gave the best yield and corresponded  
to h value under the given condition. Iron and lead  
gave very low value.



## FACTORS.

1. Influence of current on strength of precipitation.

Under same condition, by change in electrolyte, visible precipitate is obtained. See in the experiment series 6.

2. Effect of change concentration in the electrolyte.

There is an optimum concentration for the precipitation under each condition. The conditions may include current density, various cathodes, nature of electrolyte, temperature of the bath, etc. The others.

Under the condition of constant current, the concentration of 1 or 4 percent was found to be best suited.

3. Influence of the second salt solution.

As far as possible dilution of the solution of the first salt solution,

a. The presence of the second salt influences the solubility of precipitate.

b. This is true acceleration of precipitation into the incipient.

c. The ion and the minimum time of precipitation is little longer.



3. The concentration in excess of the solution  
is usually omitted.
4. As is often the case, the economy, however,  
leads to the simplification.
5. The use of soluble salts of uranium.

In industrial practice the use of soluble salt  
of uranium is less economical, owing to the high  
cost of uranium salt. By this very reason Vassiliev, the  
inventor of electrolytic method, has devised the process  
according to which, without separation of uranyl  
or the introduction of less concentrated solutions.  
As a suitable oxidant he has chosen oxygen.

The use of oxygen is difficult, as the cost of  
air, nitrogen, helium, or a combination of them, is still  
high and considerable. Another disadvantage,  
is the difficulty of the electrooxidation of uranyl salts  
which are insoluble. On the application of  
galvanic current through the uranyl solution, no change  
can take place due to the low temperature.

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